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| (54) Title: ALKOXY ALLYL (DI)PEROXIDE CHAIN TRANSFER AGENTS | | | |
| (57) Abstract | | | |
| <p>Novel unsaturated peroxides useful as molecular weight regulators in polymerization reactions are disclosed. Also disclosed are a polymerization process employing unsaturated peroxyketals as molecular weight regulators, polymers and oligomers made by this process and articles of manufacture comprising one or more polymers or oligomers made by this process. The molecular weight regulating unsaturated peroxides provide the ability to introduce a functionality to the oligomer or polymer, in a manner which gives a good monomer conversion and a minimal amount of by-products.</p> | | | |

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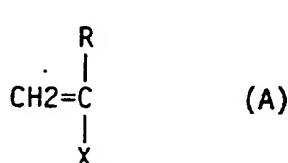
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Alkoxy Allyl (Di)Peroxide Chain Transfer Agents

5 The invention relates to novel alkoxy-functional allyl peroxides and to the application of alkoxy-functional allyl peroxides, as well as diperoxides, as chain transfer agents in the radically (co)polymerization of unsaturated monomers. The present invention also relates to methods of radically (co)polymerizing unsaturated monomers in the presence of said peroxides to thereby control the 10 molecular weights of the resulting polymers and to polymers and shaped objects containing polymers produced by the instant polymerization methods.

15 The general concept of employing a molecular weight regulating agent, also known as a chain transfer agent, as an additive during polymerization reactions has been known for a long time. A number of different chain transfer agents having an olefinic group therein, have been employed for this purpose.

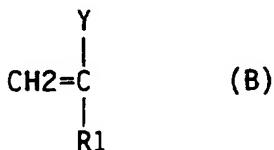
20 Perhaps one of the earlier disclosures of such a polymerization modifying material can be found in U.S. patent 3,248,374 published on 24 June 1966, wherein the use of an olefin of the formula A as a polymerization modifier is disclosed:



30 wherein R is hydrogen, halogen or a saturated aliphatic radical and X is halogen, cyanide, phenyl, carboxyl, carbonate, phenoxy, -CONH₂, -CONH-alkyl or -CON-dialkyl. The presence of these olefinic

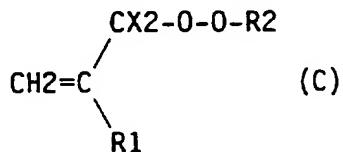
materials during the polymerization of vinylidene chloride with other olefinic materials rendered the resultant polymer more water soluble.

PCT patent application WO 88/04304 published on 16 June 1988 discloses the use of compounds of the formula (B) for the purpose of controlling the molecular weight and end group functionality of polymers.



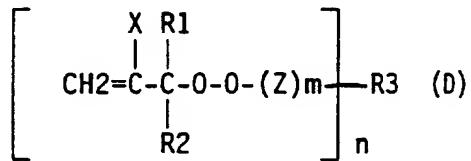
wherein R1 is hydrogen or a group capable of activating the vinylic carbon towards free radical addition; Y is OR2 or CH2X(R2)n, where R2 is an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted saturated or unsaturated carbocyclic or heterocyclic ring; X is an element other than carbon selected from Groups IV, V, VI or VII of the Periodic Table or a group consisting of an element selected from Groups IV, V or VI of the Periodic Table to which is attached one or more oxygen atoms; and n is a number from 0 to 3 such that the valency of X is satisfied and, when n is greater than 1, the groups represented by R2 may be identical or different.

PCT patent application WO 91/06535 published on 16 May 1991 discloses the use of compounds of the formula (C) for the purpose of controlling the molecular weight and end group functionality of polymers.

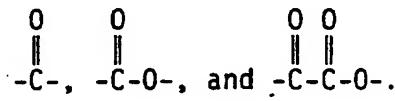


wherein R1 is hydrogen, chlorine, an alkyl group or a group capable of activating the vinylic carbon towards free radical addition; R2 is hydrogen or an optionally substituted alkyl, alkenyl, aryl, cycloalkenyl or cycloalkyl group or the group -COZ, where Z is R3 or OR3, where R3 is hydrogen or an optionally substituted alkyl, alkenyl or aryl group; and X is a hydrogen atom, an alkyl or aryl group, or a halogen, and the two X groups may be the same or different.

PCT patent application WO 91/07387 published on 30 May 1991 discloses the use of peroxides of the formula (D) as chain transfer agents in polymerization reactions.

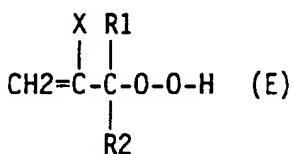


20 wherein n is an integer from 1-4, R1 and R2 are independently selected from hydrogen and lower alkyl, X is an activating group capable of enhancing the reactivity of the olefinic group towards free radical addition; R3 is part of a leaving group having a valency of n, m is 0 or 1 and Z is selected from:



These chain transfer agents may be employed in the free radical polymerization of monomers such as (meth)acrylates, styrene and its derivatives, vinyl esters, dienes, acrylonitrile and olefins.

30 PCT patent application WO 91/07440 published on 30 May 1991 discloses the use of hydroperoxides of the formula (E) as chain transfer agents in polymerization reactions.

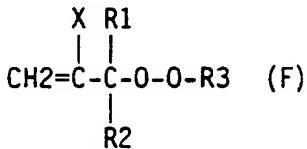


wherein R1 and R2 are independently selected from hydrogen and lower alkyl or together may form a C5-C7 aliphatic ring; and X is an activating group capable of enhancing the reactivity of the olefinic group towards free radical addition. These chain transfer agents may be employed in the free radical polymerization of monomers such as (meth)acrylates, styrene and its derivatives, vinyl esters, dienes, acrylonitrile and olefins.

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PCT patent application WO 92/06953 published on 30 April 1992 discloses the use of peroxyketals of the formula (F) as chain transfer agents in polymerization reactions.

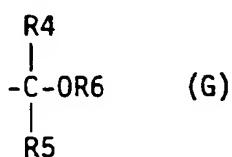
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wherein R1 and R2 are independently selected from hydrogen, lower alkyl, alkenyl and aryl; X is an activating group capable of enhancing the reactivity of the olefinic group towards free radical addition; and R3 is represented by the formula (G):

25



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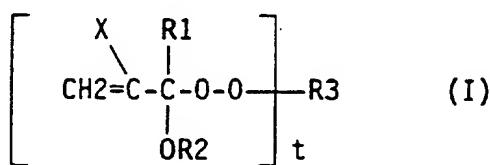
wherein R4, R5 and R6 are independently selected from optionally substituted lower alkyl, alkenyl, aryl and hydrogen, whereby R4 and R5 cannot be hydrogen together, or any two of R4, R5 and R6 may combine to form a ring. These chain transfer agents may be

employed in the free radical polymerization of monomers such as (meth)acrylates, styrene and its derivatives, vinyl esters, dienes, acrylonitrile and olefins.

5 Although many different unsaturated peroxide chain transfer agents are known, there remains a need for chain transfer agents which have good chain transfer coefficients, do not generate undesirable free radicals during polymerization reactions and which are relatively easy to produce.

10 Accordingly, it is a goal of the present invention to provide novel organic peroxide chain transfer agents which have good chain transfer coefficients, do not generate undesirable free radicals and which are relatively easy to make. This goal of the present invention is achieved by providing particular allyl peroxides useful as chain transfer agents in the radical polymerization of 15 monomers.

20 In a first embodiment of the present invention, there are provided novel alkoxy-functional allyl peroxides represented by the following formula (I):



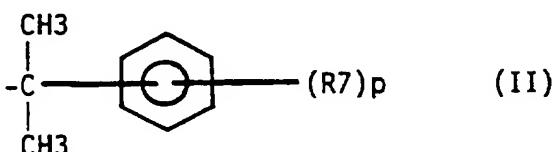
wherein $t = 1, 2, \text{ or } 3$;

30 wherein X is selected from hydrogen, C1-10 alkyl, or an activating group capable of enhancing the reactivity of the olefinic group towards free radical addition;

R1 and R2 are independently selected from hydrogen, C1-10 alkyl, C2-10 alkenyl, C6-10 aryl, and polymeric groups, or may combine to form a ring, all of which groups may be linear or branched; and

when $t = 1$,

R3 is selected from a C4-22 alkyl group, a C4-22 cycloalkyl group, a C4-22 alkylcycloalkyl group, a C4-22 cycloalkylalkyl group, a C4-22 (cyclo)alkenyl group, a C4-22 alkylcycloalkenyl group, a C4-22 cycloalkylalkenyl group, a C4-22 alkynyl, all of which groups have a tertiary structure and are optionally substituted with one or more of hydroxyl, amino, epoxy and carboxy groups; p-menthy-8-yl; pinanyl; a group of the general formula (II):



wherein p is 0, 1 or 2 and R7 is an isopropenyl group, a 2-hydroxyisopropyl group or an isopropyl group; and a group of the formula (III):



20

wherein R8, R9 and R10 are independently selected from C1-10 alkyl, C2-10 alkenyl, C6-10 aryl, all of which may be optionally substituted with one or more of hydroxyl, amino, epoxy and carboxy groups; hydrogen, or any two of R8, R9 and R10 may combine to form a ring;

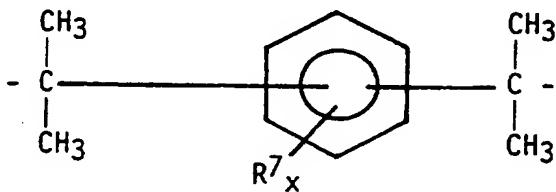
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when $t = 2$;

30

R3 is selected from a (cyclo)alkylene group, an alkylene cycloalkylene group, a (cyclo)alkenylene, an alkenylene cycloalkenylene group, a cycloalkylene alkenylene group, an alkynylene group, an alkadiynylene group, all of which groups have 4 to 22 carbon atoms and at both ends a tertiary structure; a group of the general formula:

7



wherein $x = 0$ or 1 and R^7 has the above-indicated meaning; and

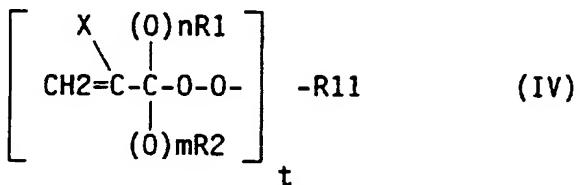
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when $t = 3$;

$R^3 = 1,2,4$ -triisopropylbenzene- $\alpha, \alpha', \alpha''$ -triyl or
 $1,3,5$ -triisopropylbenzene- $\alpha, \alpha', \alpha''$ -triyl.

10 In a second embodiment, the present invention relates to a method of radically (co)polymerizing unsaturated monomers in the presence of a polymerization initiator which employs a peroxide of the formula IV as a chain transfer agent.

15



20

wherein R_1 , R_2 , and X are as defined above; R_{11} is part of a leaving group; n is 0 or 1 ; m is 1 or 2 ; and when $m=1$, R_1 and R_2 can combine to form a ring.

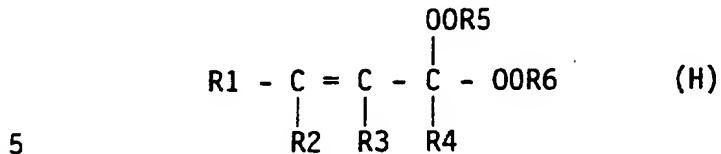
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The present invention also relates to polymers produced by the foregoing polymerization process, to shaped objects comprising one or more of such polymers, and to the use of the peroxides of the formula IV as chain transfer agents.

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Some of the compounds of the formula IV are known compounds. For example, U.S. patent 3,896,176 discloses diperoxides of the formula

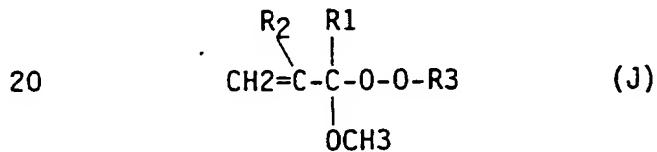
(H) and their use as initiators, cross-linkers and vulcanization agents.



wherein each of R1-R6 are selected from alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, phenyl and substituted phenyl radicals. These diperoxides are said to provide products with improved high-temperature mechanical properties, reduced low-temperature fragility and reduced solubility of the polymers in aliphatic and aromatic hydrocarbons.

10
15

In addition, the article, "Monoozonolysen von acyclischen konjugierten Dienen," Griesbaum, K. and Zwick, G., Chem. Ber., 118, pp. 3041-3057 (1985) discloses alkoxy-functional peroxides of the formula J:



wherein R1 and R2 are selected from methyl and phenyl; and R3 is selected from hydrogen and -CH₂OH. Also disclosed in this article are synthesis methods for preparing these peroxides by ozonolysis. The alkoxy-functional peroxide where R1 is methyl and R3 is hydrogen is also disclosed in, "Diozonolysen von acyclischen konjugierten Dienen in Methanol," Griesbaum, K. and Zwick, G., Chem. Ber., 119, pp. 229-243 (1986).

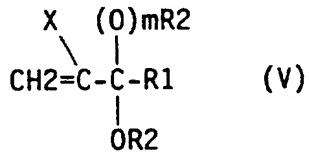
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Similar peroxidic compounds can also be found in the publications: "Monoozonolyse von 2,3-Dimethylbutadien in Pentan und in Methanol,"

Griesbaum, K. et al., *Chem. Ber.*, 116, pp. 409-415 (1983);
"Ozonolysis of Olefins Adsorbed on Polyethylene: A New Access to Ozonides by Cycloadditions of Carbonyl Oxides to Ketones," Griesbaum, K. et al., *J. Am. Chem. Soc.*, 107, pp. 5309-5310 (1985); "Products and Reaction Routes in the Diozonolysis of 2,3-Dimethyl-1,3-butadiene in Methanol," Griesbaum, K. et al., *J. Org. Chem.*, 50, pp. 4194-4199 (1985); "Reaktionen von Ozon mit 2,3-Di-tert-butyl-1,3-butadien in Lösung und auf festen Trägern," Griesbaum, K. and Volpp, W., *Chem. Ber.*, 121, pp. 1795-1799 (1988); and "Ozonolysis of Selected Vinyl Ethers," Griesbaum, K. and Kim, W.S., *J. Org. Chem.*, 57, pp. 5574-5577 (1992).

None of these publications suggest the use of the present peroxides as chain transfer agents in the radical-initiated polymerization of unsaturated monomers.

15 The alkoxy-functional peroxide compounds of the invention correspond to the above-described formula I. These peroxides, as well as the peroxides of the formula IV, may be prepared in the usual manner for similar peroxides. In preparing the peroxides of the present invention use may be made of an alkenyl derivative of
20 the general formula V:



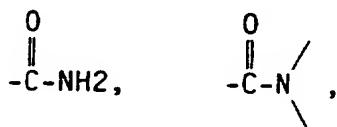
wherein X, R1, R2, and m are as defined above in either of the formulae I and IV.

30 The alkenyl derivative of the formula V may be reacted in an acid-catalysed medium with a hydroperoxide, R₃OOH or R₁ROOH, to form the alkoxy allyl peroxides and diperoxides of the formulae I or IV.

In the case that $-(O)nR2$ is OOH , compound V may be reacted with an alcohol, ether, or ketal group to introduce the necessary R3 or R11 groups.

Another useful method for the preparation of the peroxides of the present invention is to react compound V first with water to form an aldehyde compound and subsequently to react the aldehyde with a hydroperoxide to thereby introduce the group R3 or R11 thereto. Other methods of preparation can be found in U.S. Patent 3,896,176 and the articles of Karl Griesbaum mentioned above.

10 In the unsaturated peroxides of the formulae I and IV, X is an activating group capable of enhancing the reactivity of the olefinic unsaturation towards free radical addition. Preferably, X is a group selected from the group consisting of ester, acid, 15 alkoxy carbonyl, alkoxy, phenyl, substituted aromatic, aryloxycarbonyl, carboxy, acyloxy, aryloxy, aroyloxy, epoxy, carbamoyl, halogens, halocarbons,



silanes, ketones, carbonates, sulfones, sulfoxides, phosphonates, phosphine oxides, and cyano or a group including two or more of these functionalities which may be the same or different. X may 25 also combine with R1 or R2 to form a ring. In a preferred embodiment X is an electron-withdrawing group optionally having one or more functionalities such as hydroxy, carboxy, epoxy and amino.

30 The term, "electron-withdrawing", as employed herein, refers to any substituent which attracts electrons from a conjugated electron structure thereby providing a polarized resonating structure. A quantification of the level of electron-withdrawing capability is

given by the Hammett Sigma (σ) constant. This well known constant is described in many references, for instance, J. March Advanced Organic Chemistry (McGraw-Hill Book Company, New York, 1977 Edition), Pages 251-259. The Hammett constant values are positive for electron-withdrawing groups.

5 The group X may be selected on the basis of its effect on the chain transfer coefficient of the peroxide. More particularly, the ideal chain transfer coefficient is about one. Thus, for a particular peroxide, X can be selected to control the reactivity of the chain transfer agent such that the chain transfer coefficient is as close to one as possible. In this manner, the monomeric starting materials can be added in the ratio in which they are desired in the polymeric products.

15 R1 and R2 may be polymeric groups such as polyethylene oxide or polystyrene. Comb-like (co)polymers may be prepared in this way because of the polymeric chain which is already attached to the unsaturated organic peroxide when employed in the present process. The polymeric group does not hinder the unsaturated organic peroxide in its chain transfer activity.

20
25 The alkoxy-functional allyl (di)peroxides of the present invention are generally represented by the formula I given above. Particular examples of preferred R3 groups include t-butyl, t-amyl, t-pentyl, t-pentenyl, t-hexyl, t-heptyl, pinanyl, cumyl, 2,4,5-trimethylpent-2-yl, p-menth-8-yl, 4-isopropyl-1-methylcyclohexyl, 2-cyclohexylprop-2-yl, 2-methyl-2-tetrahydrofuranyl, 2-(6-ethoxy)tetrahydropyranyl, 2-tetrahydropyranyl, and 1-methoxycyclohexyl, among others. The most preferred R3 groups are t-butyl, t-amyl, t-hexyl, cumyl, and pinanyl.

The group R11 in the formula IV is a leaving group. This leaving group may include the same groups as are listed for the group R3 of the formula I and, in addition, R11 may be hydrogen. More preferred groups R11 are hydrogen and the preferred groups of R3. The most preferred R11 groups are t-butyl, t-amyl, t-hexyl, cumyl, and pinanyl.

5

As typical examples of the unsaturated peroxides which are useful as chain transfer agents according to the present invention, the following compounds may be mentioned:

3-t.butylperoxy-3-ethoxy-2-phenyl-1-propene,

10 3-t.amylperoxy-3-ethoxy-2-phenyl-1-propene,

3-t.hexylperoxy-3-ethoxy-2-phenyl-1-propene,

3-t.cumylperoxy-3-ethoxy-2-phenyl-1-propene,

3-pinanylperoxy-3-ethoxy-2-phenyl-1-propene,

3-cumylperoxy-3-methoxy-2-phenyl-1-propene,

15 3-t.butylperoxy-3-methoxy-2-phenyl-1-propene,

3-t.amylperoxy-3-methoxy-2-phenyl-1-propene,

3-t.hexylperoxy-3-methoxy-2-phenyl-1-propene,

3-pinanylperoxy-3-methoxy-2-phenyl-1-propene,

3-hydroperoxy-3-methoxy-2-phenyl-1-propene,

20 3-hydroperoxy-3-ethoxy-2-phenyl-1-propene,

3-t.butylperoxy-3-methoxy-2-methyl-1-propene,

3-t.amylperoxy-3-methoxy-2-methyl-1-propene,

3-t.hexylperoxy-3-methoxy-2-methyl-1-propene,

25 3-t.cumylperoxy-3-methoxy-2-methyl-1-propene,

3-pinanylperoxy-3-methoxy-2-methyl-1-propene,

3-t.butylperoxy-3-ethoxy-2-methyl-1-propene,

3-t.amylperoxy-3-ethoxy-2-methyl-1-propene,

3-t.hexylperoxy-3-ethoxy-2-methyl-1-propene,

30 3-t.cumylperoxy-3-ethoxy-2-methyl-1-propene,

3-pinanylperoxy-3-ethoxy-2-methyl-1-propene,

3-t.butylperoxy-3-ethoxy-1-propene,

3-t.amylperoxy-3-ethoxy-1-propene,

3-t-hexylperoxy-3-ethoxy-1-propene,
3-pinanylperoxy-3-ethoxy-1-propene,
3-cumylperoxy-3-ethoxy-1-propene,
3,3-di-t.butylperoxy-2-phenyl-1-propene,
3,3-di-t.amylperoxy-2-phenyl-1-propene,
3,3-di-t.hexylperoxy-2-phenyl-1-propene,
5 3,3-di-cumylperoxy-2-phenyl-1-propene,
3,3-di-pinanylperoxy-2-phenyl-1-propene,
3-(methoxyprop-2-ylperoxy)-3-ethoxy-2-phenyl-1-propene,
3-(2-methyl-2-tetrahydrofuranylperoxy)-3-ethoxy-2-phenyl-1-propene,
3-[2-(6-ethoxy)tetrahydropyranylperoxy]-3-ethoxy-2-phenyl-1-propene,
10 3-(2-tetrahydropyranylperoxy)-3-ethoxy-2-phenyl-1-propene, and
3-(1-methoxy-1-cyclohexylperoxy)-3-ethoxy-2-phenyl-1-propene.

15 The peroxides can be prepared, transported, stored and applied as such or in the form of powders, granules, solutions, aqueous suspensions, emulsions, pastes or any other known method. Which of these physical forms is preferred will depend on the particular polymerization system being employed. Also, considerations of safety (desensitization) may play a role. Desensitizing agents may, in fact, be used with the peroxides of the present invention and particularly suitable desensitizing agents include solid carrier materials such as silica, chalk and clay, inert plasticizers or solvents such as mono- or dichlorobenzene, and of course water.

25 The process of the present invention employs compounds of the formula IV as alternatives to known chain transfer agents for the control of molecular weight. The process of the present invention may be operated in the same manner as processes employing conventional chain transfer agents such as thiols. For example, the present process can be used in the manufacture of synthetic rubbers and other polymer formulations where reduced molecular weight aids polymer processing and improves the polymer properties.

The process is also applicable to the production of low molecular weight polymers and oligomers for a variety of applications such as for use in paints or coatings.

5 The chain transfer agents of the present invention offer several advantages. First, these materials exhibit an unexpectedly good ability to control molecular weights in polymerization processes. Thus, polymers of various molecular weights, with accurate control of the Mn, can be obtained. In its simplest form, molecular weight can be regulated by varying the amount of peroxide chain transfer agent added to the system.

10

Secondly, the method of the present invention is extremely versatile as is evidenced by the variety of polymerizations in which molecular weight regulation has been successful.

15

Thirdly, as a result of the process of the present invention, each polymer chain may be terminated by at least a bifunctional end group. This is the result of the rearrangement of the peroxide functionality to form an epoxy or ketone functionality, in combination with the carrying over of the group X from the unsaturated peroxide initiator into the end group of the formed 20 polymer or oligomer. The process of the present invention is extremely useful in producing omega-functionalized polymers, as well as alpha, omega-difunctionalized polymers. The process of the present invention is also useful in producing block- or 25 star-(co)polymers depending on the functionality of the R groups of the formula IV. These polymers and oligomers produced by the process of the present invention may be grafted onto other polymers or reacted with other monomers, polymers or oligomers to form block copolymers or graft copolymers. Such copolymers have many known 30 uses. The polymers/oligomers produced can also be involved in cross-linking reactions.

An additional advantage of the chain transfer agents of the present invention is that by chain termination of the polymer, a special type of R_{110}^{\cdot} radical is liberated. These oxygen-centered radicals readily rearrange to carbon-centered radicals thereby leading to several advantages over comparable chain transfer agents which also liberate oxygen-centered radicals on chain termination.

5

For example, oxygen-centered radicals add readily to a styrene monomer but do not add readily to acrylate monomers. This results in the retardation of the polymerization which is observed with comparable chain transfer agents. The oxygen-centered radicals released upon chain termination by the chain transfer agents of the present invention readily rearrange to carbon-centered radicals which add to both styrene and acrylate monomers, thereby resulting in a higher monomer conversion when polymerizing these monomers.

10

Due to the slow addition onto the acrylics and the excellent ability of oxygen-centered radicals to abstract hydrogen, side products are formed by prior art chain transfer agents, which side products result mainly from allylic abstraction on the peroxide, as shown by the incorporation of ethyl acrylate monomer units into the final polymer.

20

By using the peroxides of the formula IV as chain transfer agents, the oxygen-centered radicals which are liberated provide the advantage that they rearrange to carbon-centered radicals which are not good hydrogen abstractors. Thus, side products from allylic abstraction are minimal.

25

In addition, the functional end groups on the polymers or oligomers made by the process of the present invention may be changed to other functional groups by known reaction processes. For example, the epoxy functionality may simply be converted to a hydroxy functionality using known methods.

In the present process, the standard polymerization process is carried out in the presence of one or more compounds of the formula IV to thereby regulate the molecular weight of the polymer and provide functional end groups on the polymer. The reaction is generally carried out under standard polymerization conditions for the monomer being polymerized.

5

As an initiator may be used conventional polymerization initiators known in the art. The most preferred initiator will often depend upon the particular monomer which will be polymerized. In the case of styrene or methyl methacrylate polymerizations, the initiator of choice is azobisisobutyronitrile (AIBN). Generally, the amount of initiator used will be determined by known data for the particular polymerization process and will be independent of the type and amount of the chain transfer agent to be employed.

10

The chain transfer agent itself may be employed in various amounts depending primarily upon the monomer being polymerized, the chain transfer coefficient of the chain transfer agent and the desired molecular weight range to be obtained. As little as 0.001 mole percent of chain transfer agent based on the monomer can be used and up to 30.0 mole percent may also be employed. In general, from 0.1 to 15 mole percent of the chain transfer agent will produce the desired result. Of course, mixtures of different chain transfer agents may also be employed.

20

25

It is preferred to select a chain transfer agent which has a decomposition temperature above the polymerization temperature since decomposition of the chain transfer agent will prevent it from acting to regulate molecular weight. However, this need not always be the case. For example, in some instances it may be desirable for the peroxide of the formula IV to act as both a chain transfer agent and an initiator, in which case some decomposition of the peroxide chain transfer agent will be desirable.

30

Any polymerizable monomer can be used in the process of the present invention. As examples of suitable polymerizable monomers may be mentioned acrylates, methacrylates, styrene, styrene derivatives, vinyl esters, dienes, acrylonitrile, and olefins.

5 The present invention also relates to the polymers and oligomers which are formed by the process of the invention. In this respect, it has been verified by spectral analyses that these materials include an end group functionality as well as the group X. Accordingly, these oligomers and polymers are special because of the many synthetic possibilities offered by the presence of an end 10 group functionality as well as the group X.

15 The present invention also includes articles of manufacture which comprise one or more polymers or oligomers made by the process of the present invention. These articles of manufacture are useful in the coating industry, as lubricants, processing aids and interfacial agents for polymers, among other uses.

20 Finally, the present invention also includes the use of the peroxides of the formula IV as chain transfer agents in the radical-initiated polymerization of unsaturated monomers.

25 The following examples are presented to further illustrate the present invention. The chain transfer coefficient, mentioned in the examples, is calculated in the following way. The ratio of the molecular weight M_n to the molecular weight of the monomer M (M_n/M) gives DP. $1/DP$ is plotted against the ratio of the chain transfer agent (CTA) concentration to the monomer concentration ([CTA]/[Monomer]). A straight line is obtained. The slope of the 30 straight line is the chain transfer agent coefficient (Mayo equation).

Example 1

Preparation of 3-t.butylperoxy-3-ethoxy-2-phenyl-1-propene (CTA-1)

To a mixture of 0.5 mol styrene, 25 ml toluene, 2 mol aqueous NaOH-50%, and 0.5 mol% tetrabutyl ammonium hydrogen sulphate as phase transfer catalyst, 2.0 mol chloroform was dosed at such a rate that the temperature of the reaction mixture was kept between 40 and 50°C. After the addition of the chloroform the mixture was heated at 55 to 60°C until all the styrene had been converted. Subsequently, after some water was added the mixture was separated and the water layer was washed three times with toluene. The combined organic layers were dried ($MgSO_4$) and the solvent removed under vacuum in a rotavapor. The residue was distilled to give a yield of 90% 1,1-dichloro-2-phenyl cyclopropane, boiling point 63-65°C/0.2 mmHg.

15

48.0 g (1.2 mol) NaOH pellets were added to a solution of 56.1 g (0.3 mol) 1,1-dichloro-2-phenyl cyclopropane in 384.0 g (8.3 mol) ethanol. The mixture was stirred and heated to reflux during 24 hrs. The reaction mixture was allowed to cool and subsequently decanted. To the liquid phase 500 ml water was added and it was extracted with toluene, three times 100 ml and one time 50 ml. The organic layers were combined, dried over $MgSO_4$ and the solvent removed to give 52 g of 2-phenyl-2-propenal diethyl acetal (90% conversion).

25

0.5 mmol of para-toluene sulphonic acid was added to a stirred solution of 0.05 mol of 2-phenyl-2-propenal diethyl acetal in 5 ml toluene at room temperature. Subsequently, t.butyl hydroperoxide, 53% in toluene, was added dropwise in about 15 minutes. The mixture was stirred for 45 minutes after which it is washed with 10 ml water. The organic layer was dried over $MgSO_4$ and the solvent removed under vacuum in a rotavapor. CTA-1 was obtained in a yield of 80%.

Example 2

Polymerization of styrene, methyl methacrylate (MMA) and butyl acrylate (BA) in the presence of CTA-1.

Polymerization Methods

5 To a 1.0 molar solution of styrene in monochlorobenzene was added 0.5 mol% of AIBN and varying amounts of CTA-1. The polymerization was carried out in a thick-walled pyrex tube at a temperature of 80°C over a period of 60 minutes. Prior to the polymerization, the solution was degassed in order to remove oxygen. The tube was then sealed under vacuum and the polymerization carried out. The results shown in Table 1 include a control polymerization wherein no chain transfer agent was employed. The monomer conversion and molecular weights are also given in Table 1. Calculation of the chain transfer coefficient for CTA-1 for styrene polymerization yielded a
10 value of 0.41.
15

20 The same polymerization methods were employed for methyl methacrylate (MMA) and butyl acrylate (BA). The chain transfer coefficients were 0.39 for methyl methacrylate and 0.79 for butyl acrylate.
25

25 In the following table, M_n is the number average molecular weight of the polymer, D is the polydispersity ($D=M_w/M_n$) and DP_n is the degree of polymerization ($DP_n=M_n/M$) wherein M is the molecular weight of the monomer.

20

TABLE 1

Styrene

| | [CTA-1] / [monomer] | Mn | D | 1/DPn | % Conversion of Monomer |
|---|------------------------|------|------|--------|----------------------------|
| 5 | 0 | 9088 | 1.76 | 0.0114 | 10.1 |
| | 0.020 | 5081 | 1.69 | 0.0205 | 7.2 |
| | 0.037 | 3824 | 1.59 | 0.0272 | 7.5 |
| | 0.058 | 2970 | 1.51 | 0.0350 | 6.1 |

10

Methyl Methacrylate

| | | | | | |
|----|-------|-------|------|--------|------|
| | 0 | 21605 | 1.82 | 0.0046 | 47.7 |
| 15 | 0.019 | 7562 | 1.71 | 0.0132 | 39.1 |
| | 0.034 | 5215 | 1.63 | 0.0192 | 36.0 |
| | 0.053 | 3918 | 1.55 | 0.0255 | 30.3 |

Butyl Acrylate

| | | | | | |
|----|-------|-------|------|--------|------|
| 20 | 0 | 11459 | 3.60 | 0.0112 | 75.1 |
| | 0.035 | 2784 | 1.79 | 0.0460 | 42.8 |
| | 0.065 | 1894 | 1.44 | 0.0676 | 29.4 |
| | 0.100 | 1404 | 1.30 | 0.0912 | 20.9 |

25 By using NMR it was confirmed that the expected epoxide end groups were generated by these polymerization reactions.

30

Example 3

Preparation of 3-pinanylperoxy-3-ethoxy-2-phenyl-1-propene (CTA-2)

5 0.5 mmol of para-toluene sulphonic acid was added to a stirred solution of 0.05 mol of 2-phenyl-2-propenal diethyl acetal as prepared in example 1 in 5 ml toluene at room temperature. Subsequently, pinanyl hydroperoxide, 55.8% in pinane, was added dropwise in about 15 minutes. The mixture was stirred for 45 minutes after which it is washed with 10 ml water. The organic 10 layer was dried over MgSO₄ and the solvent removed under vacuum in a rotavapor. CTA-2 was obtained in a yield of 87%.

Example 4

15

20 Polymerization of styrene, methyl methacrylate and butyl acrylate in the presence of ethyl-2-[2-(1-pinanylperoxy)phenyl] propenoate (CTA-2). The same polymerization methods as used in Example 2 were employed in this example except that CTA-2 was substituted for CTA-1. The chain transfer coefficients for CTA-2 were 0.47 for styrene, 0.96 for butyl acrylate and 0.42 for methyl methacrylate. The remaining results are given in Table 2.

25

30

TABLE 2

Styrene

| | [CTA-2] / [monomer] | Mn | D | 1/DPn | % Conversion of Monomer |
|---|------------------------|------|------|--------|----------------------------|
| 5 | 0 | 9088 | 1.76 | 0.0114 | 10.1 |
| | 0.022 | 4557 | 1.51 | 0.0228 | 7.2 |
| | 0.040 | 3303 | 1.40 | 0.0315 | 6.7 |
| | 0.063 | 2537 | 1.31 | 0.0410 | 5.3 |

10 Methyl Methacrylate

| | | | | | |
|----|-------|-------|------|--------|------|
| | 0 | 21605 | 1.82 | 0.0046 | 54.2 |
| 15 | 0.017 | 7771 | 1.63 | 0.0129 | 39.8 |
| | 0.031 | 5344 | 1.53 | 0.0187 | 32.3 |
| | 0.047 | 4055 | 1.44 | 0.0247 | 25.1 |

20 Butyl Acrylate

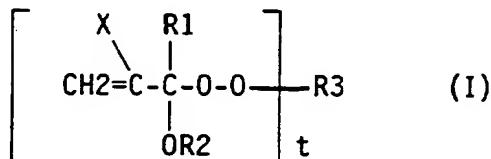
| | | | | | |
|----|-------|-------|------|--------|------|
| | 0 | 11459 | 3.60 | 0.0112 | 75.1 |
| 20 | 0.035 | 2590 | 1.44 | 0.0494 | 22.9 |
| | 0.067 | 1589 | 1.25 | 0.0806 | 12.1 |
| | 0.106 | 1140 | 1.18 | 0.1123 | 7.8 |

25 Using NMR analysis, the expected epoxide and ketone end groups were confirmed for the polymerization of butyl acrylate. The polymerization of styrene gave a polymer with ketone end groups.

30 The foregoing examples have been presented for the purpose of illustration and description only and are not to be construed as limiting the scope of the invention. The scope of the invention is to be determined by the claims appended hereto.

What is claimed is:

1. Alkoxy-functional allyl peroxides useful as chain transfer agents in the radical (co)polymerization of unsaturated monomers characterized in that said alkoxy-functional peroxides are represented by the following formula (I):



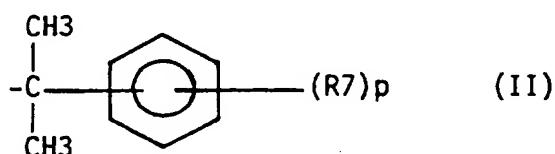
wherein $t = 1, 2, \text{ or } 3$;

15 wherein X is selected from hydrogen, C1-10 alkyl, or an activating group capable of enhancing the reactivity of the olefinic group towards free radical addition;

20 R1 and R2 are independently selected from hydrogen, C1-10 alkyl, C2-10 alkenyl, C6-10 aryl, and polymeric groups, or may combine to form a ring, all of which groups may be linear or branched; and

when $t = 1$,

25 R3 is selected from a C4-22 alkyl group, a C4-22 cycloalkyl group, a C4-22 alkylcycloalkyl group, a C4-22 cycloalkylalkyl group, a C4-22 (cyclo)alkenyl group, a C4-22 alkylcycloalkenyl group, a C4-22 cycloalkylalkenyl group, a C4-22 alkynyl, all of which groups have a tertiary structure and are optionally substituted with one or more of hydroxyl, amino, epoxy and carboxy groups; p-menthy-8-yl; pinanyl; a group of the general 30 formula (II):



5 wherein p is 0, 1 or 2 and R7 is an isopropenyl group, a 2-hydroxyisopropyl group or an isopropyl group; and a group of the formula (III):

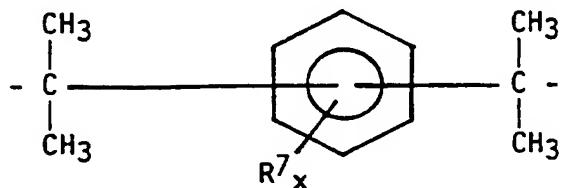


15 wherein R8, R9 and R10 are independently selected from C1-10 alkyl, C2-10 alkenyl, C6-10 aryl, all of which may be optionally substituted with one or more of hydroxyl, amino, epoxy and carboxy groups; hydrogen, or any two of R8, R9 and R10 may combine to form a ring;

when t = 2;

20 R3 is selected from a (cyclo)alkylene group, an alkylene cycloalkylene group, a (cyclo)alkenylene, an alkenylene cycloalkenylene group, a cycloalkylene alkenylene group, an alkynylene group, an alkadiynylene group, all of which groups have 4 to 22 carbon atoms and at both ends a tertiary structure; a group of the general formula:

25



30 wherein x = 0 or 1 and R7 has the above-indicated meaning; and

when t = 3;

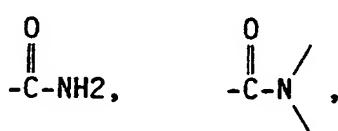
R3 = 1,2,4-triisopropylbenzene- α , α' , α'' -triyl or
1,3,5-triisopropylbenzene- α , α' , α'' -triyl.

2. Peroxides as claimed in claim 1 wherein R3 is selected from the group consisting of tertiary alkyl groups having 4-10 carbon atoms, pinanyl, and a group of the formula II; all of which groups may be optionally substituted with one or more of hydroxyl, amino, epoxy and carboxy groups.

5 3. Peroxides as claimed in claim 2 wherein R3 is selected from t-butyl, t-amyl, t-hexyl, cumyl, and pinanyl.

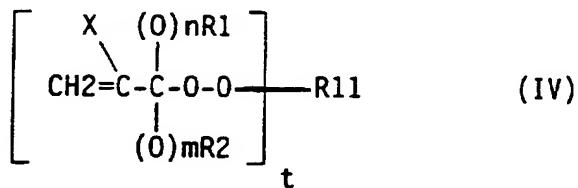
10 4. Peroxides as claimed in any one of claims 1-3 wherein X is an electron-withdrawing group.

15 5. Peroxides as claimed in any one of claims 1-3 wherein X is a group selected from the group consisting of ester, acid, alkoxy carbonyl, alkoxy, phenyl, substituted aromatic, aryloxycarbonyl, carboxy, acyloxy, aryloxy, aroyloxy, epoxy, carbamoyl, halogens, halocarbons,



25 silanes, ketones, carbonates, sulfones, sulfoxides, phosphonates, phosphine oxides, and cyano or a group including two or more of these functionalities which may be the same or different or X may combine with R1 or R2 to form a C5-C7 aliphatic ring.

30 6. A method of radically (co)polymerizing unsaturated monomers with a polymerization initiator in the presence of an effective amount of one or more peroxides of the formula (IV):



5

wherein X is an activating group capable of enhancing the reactivity of the olefinic group towards free radical addition; t, R1 and R2 are as defined in claim 1; R11 is part of a leaving group; n is 0 or 1; m is 1 or 2; and when m=1, R1 and R2 can combine to form a ring; to thereby regulate the molecular weight of the resulting polymer.

10

- 15 7. A method as claimed in claim 6, wherein from 0.001 to 30.0 mole percent of said peroxide based on the moles of polymerizable monomer, is employed.
- 20 8. A method as claimed in claims 6-7 wherein said polymerizable monomer is selected from the group consisting of acrylates, methacrylates, styrene, styrene derivatives, vinyl esters, dienes, acrylonitrile and olefins.
- 25 9. A (co)polymer produced by any one of the methods claimed in claims 6-8.
- 30 10. A shaped object comprising one or more (co)polymers produced by any one of the methods claimed in claims 6-8.
11. Use of a peroxide of the formula (IV) as a chain transfer agent in the radical initiated polymerization of unsaturated monomers to thereby regulate the molecular weight of the resulting polymer.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 96/01230

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F2/00 C08F2/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| A | WO,A,92 06953 (AKZO N.V.) 30 April 1992 cited in the application --- | |
| A | WO,A,91 06535 (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 16 May 1991 cited in the application ----- | |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

2 July 1996

Date of mailing of the international search report

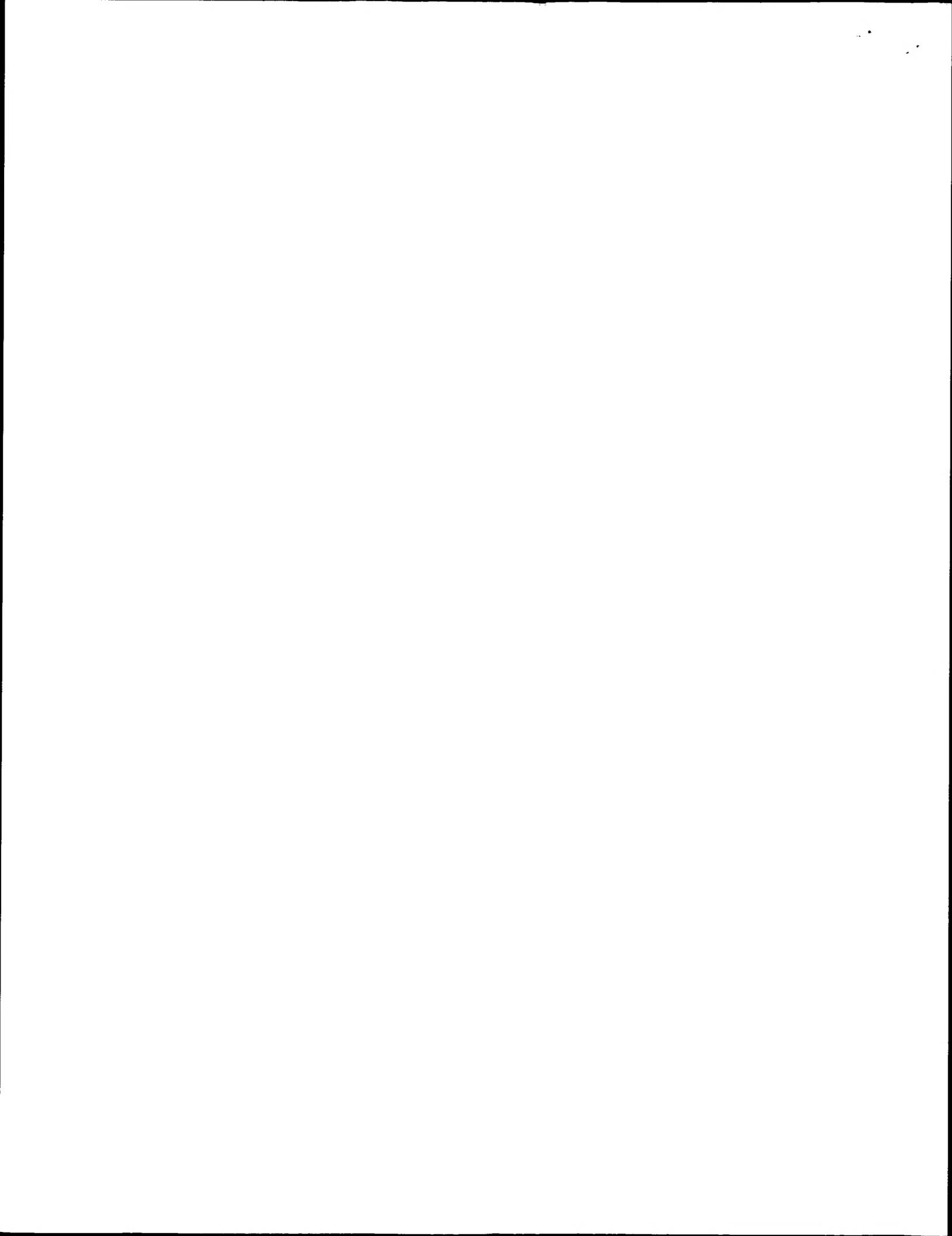
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inventor / Application No
PCT/EP 96/01230

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|--|------------------|-------------------------|----------|------------------|
| WO-A-9206953 | 30-04-92 | CA-A- | 2094155 | 17-04-92 |
| | | DE-D- | 69014899 | 19-01-95 |
| | | DE-T- | 69014899 | 14-06-95 |
| | | DE-D- | 69104055 | 20-10-94 |
| | | DE-T- | 69104055 | 02-03-95 |
| | | EP-A- | 0500624 | 02-09-92 |
| | | EP-A- | 0553185 | 04-08-93 |
| | | ES-T- | 2061269 | 01-12-94 |
| | | JP-T- | 6502142 | 10-03-94 |
| | | US-A- | 5292839 | 08-03-94 |
| WO-A-9106535 | 16-05-91 | AU-B- | 6616990 | 31-05-91 |
| | | EP-A- | 0500575 | 02-09-92 |

